

June 16, 1942.

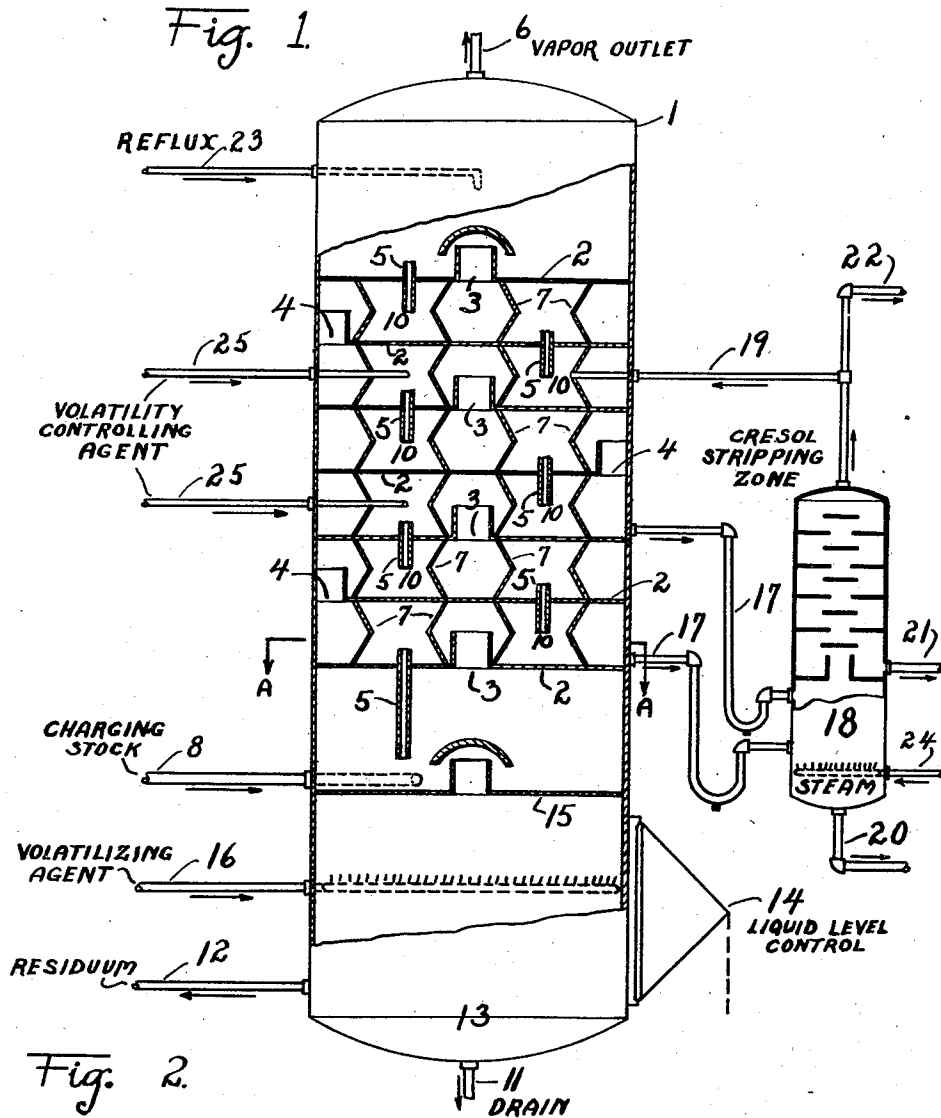
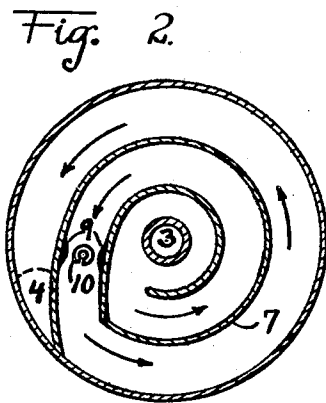
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2,286,503

PROCESS FOR SEGREGATING HYDROCARBONS

Filed June 29, 1938

2 Sheets-Sheet 1



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Fig. 3.

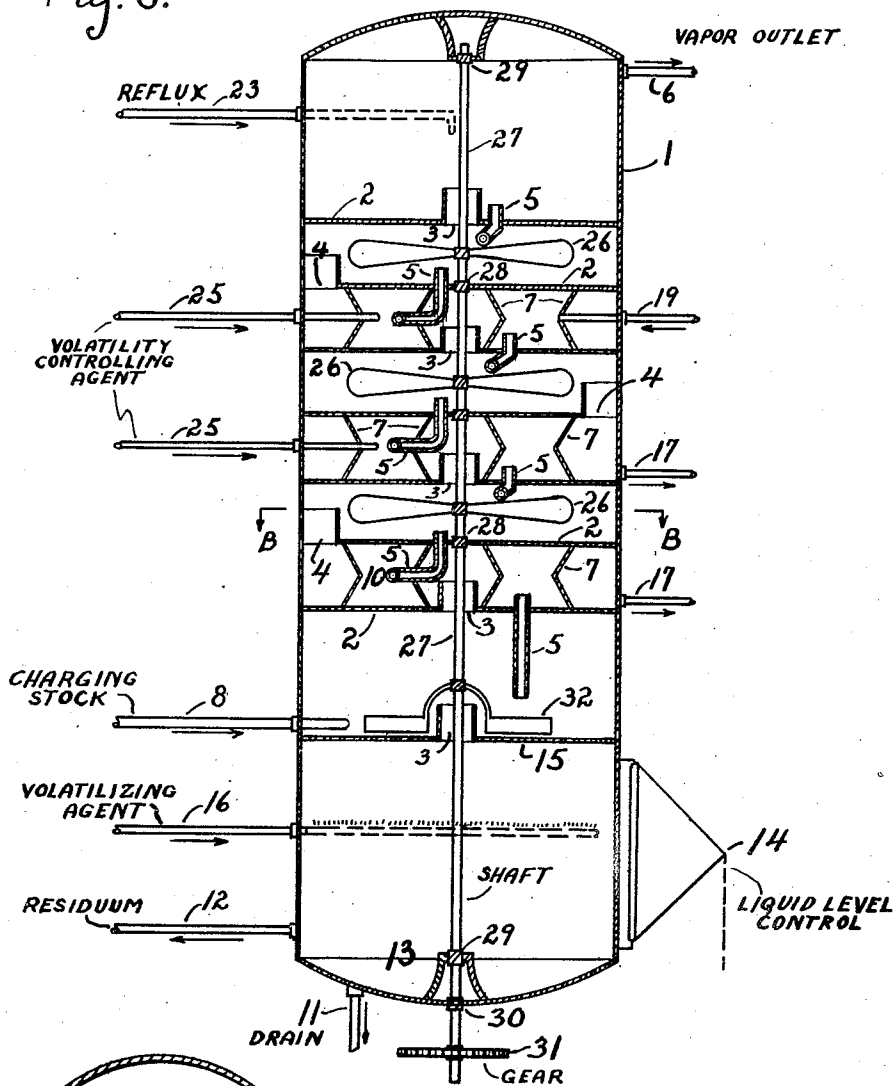
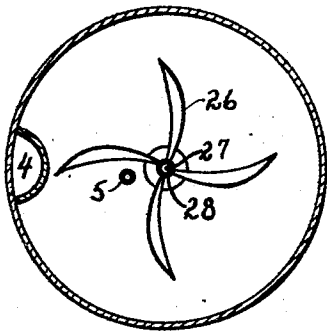


Fig. 4.

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## UNITED STATES PATENT OFFICE

2,286,503

## PROCESS FOR SEGREGATING HYDROCARBONS

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8 Claims. (Cl. 196—13)

This invention relates to a means and method for segregating from a mixture of various miscible hydrocarbons a liquid concentrate of specific components through a novel application of principles for effecting dispersion, controlling volatility, and inducing coalescence.

Until now the segregation of specific types of components or individual components from a mixture of hydrocarbons having similar physical and chemical characteristics as in crude and decomposed petroleum hydrocarbon fractions of narrow boiling range has been a difficult problem. A method of separation used primarily has been distillation. Solvent extraction is another method. While distillation is sometimes effective when carried out with precision, it is thus uneconomical when used on a large scale; hence, was tried the separation by liquid solvents calculated to have selective chemical affinities for certain components with an expectation that two distinct phases of liquid would separate by the action of gravity on account of the difference in density between an undissolved component phase and a dissolved component phase. The latter method of separation has been found impractical for intensive isolation of specific components.

I have found that simple distillation using the ordinary kinds of vapor fractionation devices, such as bubble towers and gravitational separation means, even those in which mechanical centrifuging means are used for amplifying the force of gravity, are very inefficient in overcoming the powerful intermolecular forces of attraction between the hydrocarbon components, between the solute and undissolved components, and even those between the solvent and solution for the undissolved components. I have, therefore, devised a method of separation which employs forces having magnitudes closer to those of the intermolecular forces and operates on matter maintained principally in a dispersed condition so as to weaken the intermolecular attraction between the hydrocarbon components. A very simple illustration of the manner in which my method operates can be observed in the well known distillation test for determining the quantity of water in gasoline. In this test almost a negligible quantity of water which is homogeneously dissolved in the gasoline can be segregated therefrom, not by simple distillation practice, nor by settling nor centrifuging, but by dispersing the solution into the vapor state then controlling the condensation of the vapors so that the

water molecules coalesce and condense out from the remaining hydrocarbon vapors.

An object of this invention is to obtain dispersion of mixed hydrocarbons and volatility controlling agent and to induce the proper coalescence of specific hydrocarbon components with an apparatus designed to carry out these manipulations effectively and with economy of energy, since the known kinds of vapor fractionating equipment are not satisfactorily adapted for the use of my method, and neither are the known types of centrifuges which depend for operation solely upon rapidly rotating parts. Further objects reside in the application of my method. These and other objects will become apparent from the following description and the claims.

As can be readily noted, this invention has applications of a great variety, for example, in isolating substantially pure individual hydrocarbons from a very close cut of hydrocarbons, such as refinery gas, gasoline, etc., for fractionating emulsions which easily foam in ordinary distillation, for absorbing natural gas, for dehydrating a hydrocarbon oil, for incorporating anti-detonating agents into fuels efficiently, for segregating anti-knock components from motor fuels, for segregating non-paraffinoid hydrocarbons from lubricating oils, and for fractionation of any type of mixture or solution largely composed of hydrocarbons, such as vapors from a cracking zone or crude petroleum oil.

In general the method of this invention involves the following steps: First, there is the step of dispersing the mixture to be submitted to the fractionation preferably together with a volatility controlling agent which broadly and usually is a substance normally in liquid state, partly immiscible with the hydrocarbon mixture, having somewhat greater polarity (solubility in water) than the hydrocarbons, selectively greater chemical attraction for the type of hydrocarbons intended to be segregated as a liquid concentrate, and lower volatility than the hydrocarbons to be left in the vapor state. By dispersing is meant conversion of a substance into gaseous or vapor state, into thin films on a solid contact surface, or into an atomized liquid suspended in a gaseous atmosphere. As volatility controlling agents preferably may be used one or more of the following types of substances; alcohols, such as ethyl alcohol and the higher alcohols in fusel oil, water, cresols, phenol, aniline, crotonaldehyde, carbon tetrachloride, zinc chloride, aluminum chloride, sulphur dioxide, benzene

complex, nitro-benzene, etc. Different solvents may be used at several stages; secondly, there is the step of coalescing and precipitating from the dispersion specific hydrocarbons, particularly those in which has been induced a lower volatility by a volatility controlling agent. Such hydrocarbons as are made to coalesce may do so dissolved in the volatility controlling agent or occluded by it. More particularly, these steps are used in repeated alternate succession.

The features of the apparatus considered suitably adapted for carrying out the steps of dispersing and coalescing are embodied in means for generating vapors from the hydrocarbon mixture, means for passing liquid volatility controlling agent into contact with the generated vapors at multiple stages, with the general flow of the liquid agent and the vapor streams being preferably countercurrent in direction, means for utilizing the velocity head energy of the vapors to disperse the liquid agent at each contact stage, and means for altering the velocity and path of the stream containing dispersed hydrocarbons and agent in a manner which accelerates the intended coalescing and precipitation.

For clarity, the invention will be described by reference to a diagrammatic showing of a preferred form which the apparatus may take. In the drawings are represented two views of an apparatus.

Figure 1 shows an elevational view of tower 1 and appurtenances, a cutaway section of the tower being shown to illustrate the internal structure.

Figure 2 shows a horizontal cross sectional view of tower 1 at the section indicated by line A—A in Figure 1.

Figure 3 shows an elevational view of modified tower 1 in which a rotating agitation is used to aid dispersion and centrifugal action in stages.

Figure 4 shows a horizontal cross sectional view of modified tower 1 at the section indicated by line B—B in Figure 3.

The tower 1 consists in a multiplicity of sections separated by superimposed plates 2, each plate being provided with vapor passage means 3 and 4, interconnecting the sections and liquid removal means, such as overflow pipes 5. Between each pair of successive plates a lateral spiral fluid passage is formed by stationary curved impingement vanes 7, which are best viewed in a horizontal cross-section, as shown in Figure 3. These vanes may be broadly described as sets of concentric and somewhat cylindrical tubes partitioning the fluid passages in each section and containing ports 9 and 10, for making the passages continuous, the ports numbered 10, being constricted and provided with orifice inlets from adjoining liquid overflow pipes to act as atomizers. At the upper end, tower is equipped with a vapor outlet pipe 6, leading to any type of conventional vapor condensing, collecting, or further fractionating means, and a fluid inlet pipe 8, for feeding fluid charging stock. At the extreme base of the tower are drain outlets 11 and 12, the former for any residuum collected in the settling zone 13, of the tower 1, and the latter for decanting cleaner residuum from which sludge is settled out. A liquid level control means 14, may be used to control flow in either or both drain outlets. Between the bottom plate 2, and the residuum settling zone at base of the tower are a tangentially injecting inlet pipe 8, for the charging stock, a perforated retaining pan 15, for retain-

ing liquids in a rotary motion caused by the tangential injection of charging stock and a vapor inlet jet 16, located so as to contact the jetted vapors with liquids which drip from the pan 15. The pan and tangential injection arrangement is particularly useful when the injected hydrocarbons are partly in liquid state, for it acts to retain the liquids for a period to permit increased vaporization, the vapor jet underneath acting further to strip the residual portions which drip from the pan. Condensed liquids which collect on the plates may be removed at any or all of the several stages by withdrawal lines 17, which can be two or more and led thereby to receivers or to an auxiliary settling and stripping zone 18, from which the volatility agent, if of relatively high volatility, is distilled as overhead through line 22, and a portion being returned through line 19, if desired, or, if of relatively low or intermediate volatility, it may be withdrawn as a bottom product by line 20, or as a side-draw product by line 21, the liquid hydrocarbon concentrate being removed in an alternate manner, depending in turn on its relative volatility. Overhead from the auxiliary stripping column may be passed by pipe 19, into an intermediate part of tower 1, or by pipe 22, to a condenser and receiver or other separating means (not shown). A reflux from the overhead of tower 1, may be returned thereto for regulating conditions in the tower by pipe line 23. By means of inlet lines 25, additional volatilizing fluids such as steam, gaseous hydrocarbons etc., and/or volatility controlling agents may be injected at suitable temperatures into the spiralling stream of fluids to increase the stream velocity and control the volatilities of the substances dispersed in the stream while permitting a desired amount of condensation at each stage in the tower.

In Figure 3, the modified tower 1 illustrates the same general arrangement as shown in Figure 1, except that the corresponding tower in Figure 3 has provisions for mechanically rotated impingement vanes 26, in place of stationary vanes 7, disposed in some sections between pairs of plates 2. The rotating vanes 26 are attached to a rotating shaft 27, which passes vertically through the central axis of tower 1. The vanes 26, may be two or more in number and are preferably designed as illustrated in Figure 4, to add velocity to the vapor stream in place of fluid injectors or with the fluid injectors, to simultaneously disperse liquids from upper plates into the vapor stream and to centrifuge coalesced liquids out of the vapor stream. Shaft 27, rotates in journals 28, and sockets 29, and protrudes through a packed fitting 30, in the base to a means for rotating said shaft such as for example a driven gear 31, or by any other suitable manner. Additional circulatory turbulence in pan 15, may be produced by vanes 32, attached to shaft 27, and rotated therewith.

As an illustration of a method for operation in which cyclic hydrocarbons and asphaltic substances are to be segregated as a liquid concentrate from more desirable paraffinic lubricating constituents in a mixture containing those types of compounds the following example is given:

An initial charging stock e. g. a naphthene base bright stock, at a temperature of about 450 to 650° F., is led into the tower 1, by inlet 8, in admixture with about an equal or larger proportion of cresols and subjected to vaporization in tower 1, at a pressure maintained sufficiently

low to obtain vaporization of a substantial part of the hydrocarbons and the cresols at a pressure of about 200 to 700 mm. mercury absolute. A small proportion of gaseous hydrocarbons, steam, or other gaseous volatilizing agent may be introduced by pipe 16. Hydrocarbon and cresol vapors thus produced in the lower part of the tower flow into the continuous spiral passages formed between the plates 2, by the circular impingement vanes 7.

At each stage of swirling motion between pairs of plates the more aggregated molecules of the cresols, cyclic hydrocarbons and asphaltic components of the mixture, due to their higher inertia and lower fugacity, are precipitated out against the walls of the impingement vanes and collected as a liquid layer above each plate. One portion of the liquid layers passes down through the overflow pipes 5, from which the down-flowing liquid is aspirated by a constricted high velocity fluid stream at points 16 and becomes thereby redispersed. Another portion of the liquid layers is withdrawn from one or more plates by pipes 17, as a liquid concentrate of denser hydrocarbons mixed with some of the cresols and is removed to a cresol stripping zone 18, in which the cresols are volatilized for example, by addition of a small amount of steam, which is injected by pipe 24. Instead of cresols there may be similarly employed high boiling polar compounds with relatively higher affinity for cyclic hydrocarbons and asphaltic substances than for paraffinic compounds. Such polar compounds may be selected from the following group: nitroaniline, aniline, chloronitrobenzene, nitrobenzene, nitroanisole, tetrahydronaphthalene, benzyl alcohol, triacetin, diacetin, and other similar agents having higher affinity for cyclic hydrocarbons than for paraffinic compounds.

As a further example, denser molecules are separated from cracked naphtha introduced near the bottom of tower 1, by inlet pipe 3, at a temperature in the range of 400 to 600° F., and mixed in their spiral paths up through said tower with fusel oil alcohol vapors having a temperature of about 200° F., or higher injected by pipe 25, preferably in about equal proportions by weight to the weight of the charged hydrocarbons. A minor quantity of steam at a temperature of about 400° F., or higher is injected at the jet discharge of inlet 16. The vapors nearing outlet 6 are maintained at a temperature of about 350° F., with the pressure in the tower being substantially atmospheric or slightly varying below or above atmospheric pressure depending upon the desired end point for the overhead fraction. The overhead vapors highly enriched in lighter and more paraffinic hydrocarbons may be passed together with residual steam to a fractionating tower wherein they are fractionated to procure relatively heavy reflux before final condensation so that a portion of said heavy reflux may be recycled to the upper part of tower 1, through pipe 23, for control of the overhead vapors. Portions of the liquid aggregate collected on intermediate plates 2 and comprising mainly a mixture of alcohols and hydrocarbons of cyclic branched or unsaturated character are withdrawn from the side of tower 1, by means of pipes 17, to side stripper 18, in which they are refractionated in the presence of a small quantity of steam to cause the hydrocarbons and steam to pass overhead through pipe 22, to a condenser thence a separator in which a concentrate of hydrocarbons separated out as a liquid layer from a water

layer, said concentrate of hydrocarbons being rich in hydrocarbons of cyclic branched or unsaturated character. Liquid bottoms withdrawn from the base of tower 18, are largely composed of alcohols while side draws which may be removed from an intermediate plate by pipe 21, from stripper 18, are composed largely of alcohol and hydrocarbons which may be further fractionated to further separate hydrocarbons from alcohol as described with respect to the stripping action in stripper 18.

Among some of the advantages which may be ascribed to the novel method and apparatus of this invention are:

1. Economic construction of an efficient fractionating means for segregating specific components from a mixture of hydrocarbons, with elimination of several defects commonly found in packed towers or bubble towers by:

- (a) Having a low pressure drop
- (b) Avoiding channeling
- (c) Avoiding flooding
- (d) Having less liquid holdup
- (e) Being smaller in size for a given capacity
- (f) Having less dead spaces and
- (g) Imposing closer to equilibrium conditions

2. More efficient separation with conservation of energy by:

- (a) Intimate contacting of dispersed materials
- (b) Using the velocity head in the fluid stream for atomizing liquids and forcing liquids from higher to lower levels in the fractionating tower and
- (c) Lateral centrifuging of vapors with entrained liquid particles to throw particularly the heavier particles out of the vapor stream.

It is to be understood that the apparatus may be equipped with suitable indicating or recording devices for observation of pressures, temperatures, flow, etc., and that the apparatus is insulated where desired to maintain heat, and with valves and pumps to regulate flow as required. The invention is not to be limited to the particular form of apparatus herein described nor by any specific example or theory used for the purpose of illustration.

Having described my invention, what I claim and desire to secure by Letters Patent, is as follows:

1. The method for segregating a liquid concentrate of specific hydrocarbons from a mixture of hydrocarbons, which comprises dispersing into a vapor stream the mixed hydrocarbons in the form of liquid particles together with a volatility controlling compound having greater chemical attraction for the specific hydrocarbons to be segregated, said vapor stream flowing upwardly and through a series of spiral passages, and coalescing said specific hydrocarbons together with volatility controlling agent by centrifugal action on said vapor stream carrying concurrently suspended therein the dispersed liquid particles.

2. The method for segregating a liquid concentrate of specific hydrocarbons of non-paraffinoid properties from a mixture of hydrocarbons, which comprises partially vaporizing said mixture, dispersing into a vapor stream liquid particles of an unvaporized portion of the mixed hydrocarbons together with a volatility controlling compound having greater chemical attrac-

tion for the non-paraffinoid hydrocarbons to be segregated, centrifuging the dispersion to coalesce non-paraffinoid hydrocarbons and associated volatility controlling compound in liquid pools over which the vapor stream is spirally passed, and withdrawing the non-coalesced dispersed hydrocarbons of paraffinoid character in vapor phase.

3. The method for segregating a liquid concentrate of specific hydrocarbons having relatively higher density from a mixture of hydrocarbons containing hydrocarbons of lower density, which comprises dispersing into a vapor stream discrete liquid particles of said mixture of hydrocarbons with partial vaporization of the hydrocarbons in admixture with a non-hydrocarbon organic compound having greater affinity for the denser hydrocarbons of said mixture, and coalescing denser hydrocarbons together with non-hydrocarbon organic compound thus dispersed into liquid pools by imposing centrifugal forces upon the dispersion in a spiral flow.

4. The method recited in claim 3, in which a substituted cyclic hydrocarbon is used as the nonhydrocarbon organic compound and the specific hydrocarbons of relatively higher density are cyclic hydrocarbons.

5. The method recited in claim 3, in which an alcohol is used as the non-hydrocarbon organic compound and the hydrocarbons of lower density are straight chain paraffins.

6. The method recited in claim 3, in which aniline is used as the non-hydrocarbon organic compound.

7. The method for segregating a liquid concentrate of specific hydrocarbons having relatively higher density from a mixture of hydro-

carbons containing hydrocarbons of lower density, which comprises partially vaporizing a substantial portion of the hydrocarbon mixture, leading the vapors through a series of spiral passages guided by an impingement surface against which denser particles are forced out by centrifugal action and caused to coalesce into a series of liquid aggregates of varying densities, redispersing portions of said liquid aggregates into said spiralling vapor stream, and withdrawing other portions of said liquid aggregates as liquid concentrates of the specific hydrocarbons having relatively higher densities, and separating vaporized hydrocarbons of lower density.

8. The method for segregating a liquid concentrate of specific hydrocarbons having relatively higher densities from a mixture of hydrocarbons containing hydrocarbons of lower density, which comprises vaporizing a substantial portion of the hydrocarbon mixture, leading the vapors through a series of spiral passages guided by an impingement surface against which liquid particles are forced out by centrifugal action imparted to the vapor stream and caused to coalesce into a series of liquid pools, redispersing portions of said liquid pools into said spiralling vapor stream as discrete liquid particles together with a volatility controlling compound having greater chemical attraction for the specific hydrocarbons to be segregated, withdrawing portions of said liquid pools as liquid concentrates of the specific hydrocarbons having relatively higher densities, and separating vaporized hydrocarbon of lower density.

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